Application of sorption isotherm - sequential extraction analysis to the investigation of heavy metals binding by soil Fe-Mn oxides

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Interaction of heavy metals (HM) with Fe and Mn oxides significantly affects their mobility and bioavailability in soils. Although oxides are the excellent scavengers for metals, such association does not guarantee long term immobilization of contaminant metals. Under anoxic condition Fe-Mn oxides are thermodynamically unstable, leading to a release of adsorbed metals in the soil solution. Consequently, HM adsorbed onto Fe-Mn oxides in oxidizing condition may serve as a source of bioavailable metals under the lowering Eh.

Combined sorption isotherm - sequential extraction method was used to compare the role of Fe-Mn oxides and other soil constituents in Cu and Zn binding for different pollution level. This method combines the sorption isotherm and sequential extraction methods and was originally applied (Pampura *et al.*, 1993) to characterise HM binding and partitioning in Chernozem. Later this method was used by Salim *et al.* (1996) under the name Combined Sorption Isotherm - Sequential Extraction Analysis to analyse HM retention in Landfill Liners. This technique involved equilibrating the soil (Chernozem) samples (10 g) with solutions (100 ml) containing varying amounts of metals (Cu - 0 - 700 mg/kg soil, Zn - 0- 1250 mg/kg soil) and subsequently carrying out sequential extraction procedure (Tessier *et al.*, 1979) to characterise forms of metal (M) adsorbed (Exchangeable (M_{Ex}); Extractable by CH_3COOH/CH_3COONa, pH 5 (M_{AcNa}); Bound to organic matter (M_{OM}); Bound to Fe and Mn oxides (M_{Fe+Mn}); Residual (M_{Res})). Metals concentrations in the initial and final solutions were determined by flame atomic absorption spectrophotometry using standard addition technique.

This approach gives an opportunity to construct

TABLE 1. Description of Cu and Zn fractions accumulation in soil by Langmuir and Freundlich equations

Fraction	Freundlich $S_M = kC_M^p$			Langmuir $S_M = S_m(1+1/KC_M)$		
	k	p	error	K	S_m	error
Cu_{Ex}	605	1.45	0.58	–	–	–
Cu_{AcNa}	1877	1.41	0.02	–	–	–
Cu_{Fe+Mn}	2500	1.12	0.35	–	–	–
Cu_{OM}	46	0.59	0.21	2300	1.13	0.18
Cu_{Res}	3.5	0.40	0.09	5850	0.24	0.08
Bulk sorption isotherm	1830	0.97	0.63	50	62.0	0.63
Zn_{Ex}	11.5	0.77	0.27	7.85	4.46	0.26
Zn_{AcNa}	1.10	0.38	0.14	66.9	0.51	0.16
Zn_{Fe+Mn}	2.08	0.38	0.47	67.7	0.98	0.34
Zn_{OM}	0.76	0.44	0.04	47.2	0.32	0.02
Zn_{Res}	0.14	0.17	0.08	4500	0.07	0.09
Bulk sorption isotherm	13.1	0.60	0.76	17	5.26	0.43

S_M - M sorbed (meq/100 g of soil); C_M - M concentration in the solution (mM);
S_m - sorption maximum; K, k, p - constants; error - residual error (Pollard, 1982)

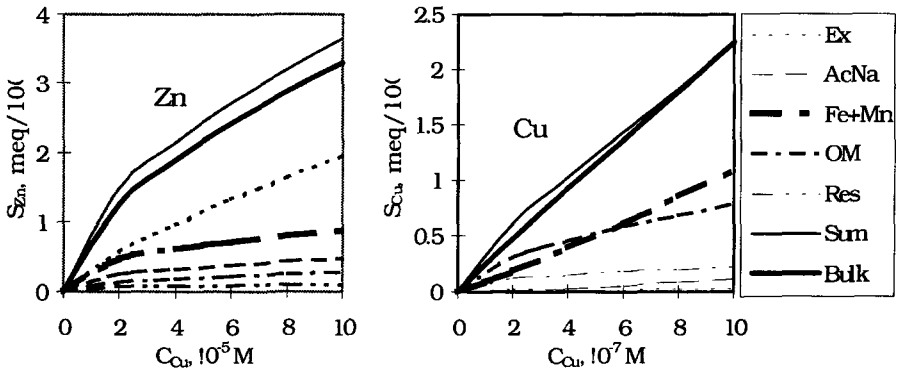

FIG. 1. Comparison of Cu and Zn accumulation in Bound to Fe and Mn oxides and other soil fractions: Ex - Exchangeable, AcNa - Extracted by CH_3COONa/CH_3COOH, pH 5, Fe+Mn - Bound to Fe and Mn oxides, OM - Bound to organic matter, Res - Residual, Bulk - Bulk sorption isotherm; Sum - Sum of five fractions $S_M = \Sigma f_i(C_M)$.

adsorption isotherm not only for bulk soil sample, but for individual soil constituents and determine sorption characteristics for individual components while together in a natural soil. Experimental Cu and Zn sorption isotherms for bulk soil and for individual soil constituents were described by Langmuir and Freundlich equations (Table 1 and Fig. 1).

Sorption of Zn onto Fe and Mn oxides can be adequately described by both Freundlich and Langmuir equations. Langmuir constants, characterising the strength of Zn bounding increased in the row $Zn_{Res} > Zn_{Fe\text{-}Mn} > Zn_{AcNa} > Zn_{OM} > Zn_{Ex}$. Sorption maximum, characterising adsorption capacity increased in the following row: $Zn_{Ex} > Zn_{Fe\text{-}Mn} > Zn_{AcNa} > Zn_{OM} > Zn_{Res}$. By contrast, Cu adsorption onto Fe-Mn oxides increased with increasing total Cu concentration and did not fit Langmuir equation. Copper adsorption isotherm can by described by equation $S_{Cu} = kC_{Cu}^p$ with $p > 1$. Percentage of Bound to Fe and Mn oxide fraction increased from 0.4% to 47.5% for Cu and from 33% to 36.6% for Zn as the amount of metal sorbed increased.

Results indicated that Fe and Mn oxides played significant role both in Cu and Zn accumulation in soil in spite of the fact that metals sorption behaviour and partitioning differed considerably.

References

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